Letters to the Editor

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INVESTIGATION ON RAMAN AND INFRARED SPECTRA OF TWO ISOMERIC AROMATIC NITRILES IN DIFFERENT STATES.

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The Raman spectra of a few organic nitriles in the solid state at −180°C were studied earlier (Bishui 1948; Deb, 1961; Deb and Mukherjee, 1963). It has been observed from the results that the lines due to $C \equiv N$ vibrations in each case undergo changes and in some cases a few low frequency Raman lines appear in the spectra with the solidification of the liquids at low temperatures. Later, Deb (1963) concluded from the results of investigation of the Raman spectra of a large number of organic compounds that certain vibrational modes perpendicular to the benzene ring shift to low frequency region due to the intermolecular association in the crystal lattices of the compounds at low temperatures. In the present work similar investigation has been made in the case of two aromatic nitriles viz, ortho and paratolunitriles in order to find out how the local field surrounding the $C \equiv N$ bond is affected in the solid state in the case of the two molecules due to the presence of CH_3 group in the benzene ring. The infrared spectra of the two compounds in the pure state and in solutions in some suitable solvents have also been studied in order to find out how the results support the above view.

RESULTS AND DISCUSSIONS

The observed Raman shifts of the compounds in the liquid and solid states at −180°C are tabulated in Tables I and II. The states of polarisation of the Raman lines of the liquids are indicated by the usual letters '*P*' and '*D*' which mean partially polarised and totally depolarised respectively.

TABLE I

Raman and infrared spectra of ortho-tolunitrile

Raman shifts in cm^{-1}			Infrared bands in cm^{-1} (Present authors)
Liquid Landolt-Bornstein Table (1951)	Liquid at 30°C Present authors	Solid at −180°C Present authors	
		80 (1)	
150 (10b)	150 (6) D	155 (4b)	
169 (8)	163 (8) D		
217 (4)	223 (1b)	242 (0b)	
342 (1)			
385 (1)			
457 (8)	460 (6) D		
	541 (3) D		
587 (3)	583 (0)		
	638 (1) P		
715 (9)	718 (8) P	720 (2)	708 (ms)
761 (2)			760 (vs)
819 (3)			942 (vw)
991 (1)			
1045 (8)	1048 (8) P	1048 (2)	1038 (w)
1108 (2)			1108 (w)
1159 (5)	1158 (2) D		1160 (w)
1208 (10)	1210 (8) P		1210 (w)
		1219 (6)	
1287 (1)			1290 (w)
1378 (4)	1381 (0b)		1385 (w)
			1440 (ms)
			1450 (ms)
1486 (3)			1488 (ms)
	1509 (0)		
1571 (3)			
1599 (9)	1600 (8) P	1602 (6)	1600 (ms)
2225 (10b)	2226 (15) D	2226 (0)	2238 (s)
2922 (1)	2925 (4b) P		2922 (w)
3050 (3)	3057 (6) D		3040 (w)
3070 (2)	3067 (4) D	3060 (0)	3070 (w)

TABLE II

Raman and Infrared spectra of para tolunitrile

Raman shifts in cm^{-1}			
Liquid Landolt-Börnstein Table (1951)	Liquid at 30°C Present authors	Solid at −180°C Present authors	Infrared bands in cm^{-1} (Present authors)
		88 (4)	
161 (7)	160 (6) D	155 (0)	
252 (3)	255 (1) P		
345 (1)			
410 (4)	407 (4) D	407 (0)	
437 (1)			
516 (0)			
549 (3)	556 (1)		
648 (4)	652 (6) D	652 (0b)	
705 (1)	705 (0)		704 (w)
797 (2)			
819 (3)	824 (6) P	824 (6)	818 (vs)
			946 (vw)
1020 (0)			1022 (w)
			1040 (w)
			1100 (vw)
			1120 (w)
1172 (10)	1180 (8) P	1180 (8)	1180 (ms)
1194 (4)	1194 (2) P		1200 (vw)
			1280 (w)
1309 (0)			
1378 (2)	1383 (2) P		1385 (w)
			1412 (w)
1445 (0)	1453 (0)		1450 (ms)
			1508 (ms)
	1517 (0)		
1604 (10)	1609 (10) D	1609 (8)	1610 (s)
2228 (10)	2230 (15) P	2227 (6)	
			2242 (s)
2875 (2)	2880 (1)		2875 (w)
2926 (1)	2929 (2)		2930 (ms)
3048 (4)			3050 (w)
	3063 (2b) D	3063 (0b)	

(a) *Changes in the Raman spectra with solidification of the liquids* :

It can be seen from the Tables I and II that in the solid state at −180°C the line 163 cm^{-1} of ortho tolunitrile and 160 cm^{-1} of para tolunitrile representing probably the out-of-plane bending vibration of C N bond appear to split up into two component in each case The line 163 cm^{-1} splits up into two lines with components at 155 and 80 cm^{-1} and the line 160 cm^{-1} splits up into two lines 155 and 88 cm^{-1} respectively. The splitting up of the lines 163 and 160 cm^{-1} due respectively to ortho and paratolunitriles is owing to weak molecular association of different strengths in the crystal lattices at low temperatures. The lines 460 and 2226 cm^{-1} due to orthotolunitrile assigned respectively to C ≡ N deformation and C N stretching oscillation of the molecule become weak with the solidification of the liquid Similar changes in the intensity of the frequency 407 cm^{-1} due to C N deformation oscillation and that of the line 2230 cm^{-1} due to C ≡ N stretching oscillation were also observed in the case of the para isomer. The change in intensity of the frequencies of C N bond is more pronounced in the case of ortho isomer than in the case of para isomer. The fact indicates stronger molecular association through C N group in the case of ortho isomer than in the case of para isomer. Also the line 1210 cm^{-1} due to ortho tolunitrile representing probably the CH bending oscillation in CH_3 group shifts to 1219 cm^{-1} under similar condition. In addition to the above changes some other frequencies due to different modes of the two molecules undergo changes at low temperatures which further support the above view.

(b) *Changes in infrared spectra in solutions*

It is observed from the infrared spectra of ortho and para-tolunitriles in the pure state and in their solutions in the solvents (polar and non-polar) that the intensity and position of the C N band are slightly affected in different polar solvents while in non-polar solvents no such changes are observed The results fairly agree with those reported earlier in the case of other nitriles (Brown, 1958, Bayliss *et al.* (1959:). However, the shift of the frequency due to C ≡ N vibration is more pronounced in the case of ortho isomer than in the case of para isomer, which may be due to weak perturbation of the local field of the C ≡ N group in the case of ortho isomer in polar solvents.

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